Oxygen Nucleophiles as Reaction Partners in Photoinduced, Copper-Catalyzed Cross-Couplings: O-Arylations of Phenols at Room Temperature

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Supporting Information

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I. General Information

The following reagents were purchased and used as received, unless otherwise specified: CuI (99.999%; Aldrich; 98% and 99.5% have also been used and provided equivalent yields), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; Aldrich), KO*t*-Bu (Aldrich), phenol (Aldrich), *p*-cresol (Aldrich), 4-phenylphenol (Alfa Aesar), 4-fluorophenol (Aldrich), 4-(2-hydroxyethyl)phenol (Aldrich), 3-methoxyphenol (Aldrich), ethyl 3-hydroxybenzoate (Aldrich), 3,5-dimethylphenol (Aldrich), 2-methoxyphenol (Aldrich), 2,4,6-trimethylphenol (Aldrich), iodobenzene (Aldrich), 1-*tert*-butyl-4-iodobenzene (Aldrich), ethyl 4-iodobenzoate (Alfa Aesar), 1-(4-iodophenyl)ethanone (Aldrich), 3-iodoanisole (Alfa Aesar), 3-iodobenzonitrile (Alfa Aesar), ethyl 3-iodobenzoate (Aldrich), 1-iodo-3,5-dimethylbenzene (Aldrich), ethyl 2-iodobenzoate (Aldrich), 2-iodo-1,3,5-trimethylbenzene (Aldrich), 1-iodonaphthalene (Aldrich), 5-iodo-1,3-benzodioxole, 2-iodopyridine (Aldrich), and 3-iodotoluene (Aldrich).

Acetonitrile was deoxygenated and dried by sparging with nitrogen, followed by passage through an activated alumina column (SG Water) prior to use.

All reactions were carried out in a Luzchem LZC–4V photoreactor at 254 nm (UVC lamps).

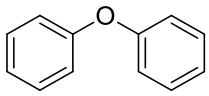
^{1}H NMR data were collected on a VARIAN 500 MHz spectrometer at ambient temperature. GC analyses were carried out on an Agilent 6890 Series system with a DB–1 column (length 30 m, I.D. 0.25 mm) and an Agilent 6850 Series system with a G-TA column (length 30 m, I.D. 0.25 mm) and a BETA DEX 120 column (length 30 m, I.D. 0.25 mm).

II. Photoinduced, Copper-Catalyzed O-Arylations

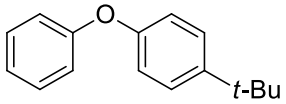
General Procedure. In air, the phenol (1.0 mmol), CuI (19 mg, 0.10 mmol), and KO*t*-Bu (56 mg, 0.50 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. The quartz tube was fitted with a rubber septum, the joint was wrapped with electrical tape,

and the quartz tube was evacuated and backfilled with nitrogen (3 cycles). DBU (154 mg, 1.0 mmol), the aryl iodide (1.2 mmol), and CH_3CN (6.5 mL) were added in turn via syringe. Then, the quartz tube was detached from the nitrogen line, and the puncture holes in the septum were immediately covered with vacuum grease. The resulting mixture was stirred for 5 minutes, and then the tube transferred to a Luzchem LZC–4V photoreactor (a Honeywell UV100A1059 UV Surface Treatment System, which can be purchased for ~$160 from common vendors such as Amazon.com, can also be used), where it was irradiated at 254 nm (UVC lamps) for 12 hours. Next, the reaction mixture was passed through a long plug of silica gel (monitored by TLC), the solvent was removed, and the residue was purified by column chromatography.

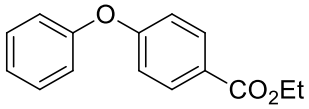
Notes: The test tube was situated in the rotating carousel in the photoreactor such that the reaction mixture was adequately stirred. If the aryl iodide was a solid, it was added after the addition of KO*t*-Bu and before purging the quartz tube with nitrogen.



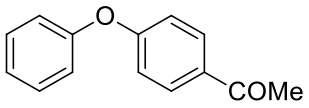
Diphenyl ether [101-84-8]. **Table 2, entry 1:** The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Colorless liquid. First run: 138 mg (81%). Second run: 136 mg (80%).



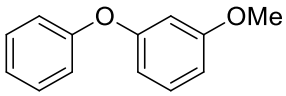
4-*t*-Butylphenyl phenyl ether [101-84-8]. **Table 2, entry 2:** The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and 1-*tert*-butyl-4-iodobenzene (213 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Colorless liquid. First run: 140 mg (62%). Second run: 145 mg (64%).



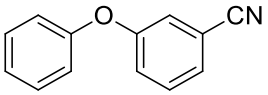
Ethyl 4-phenoxybenzoate [31994-68-0]. **Table 2, entry 3:** The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and ethyl 4-iodobenzoate (208 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by chromatography on silica gel (1%→10% dichloromethane/hexane). Colorless oil. First run: 170 mg (70%). Second run: 175 mg (72%).



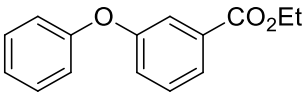
4'-Phenoxyacetophenone [5031-78-7]. Table 2, entry 4: The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and 1-(4-iodophenyl)-ethanone (301 mg, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by chromatography on silica gel (10% EtOAc/hexane). Colorless oil. First run: 156 mg (74%). Second run: 154 mg (73%).



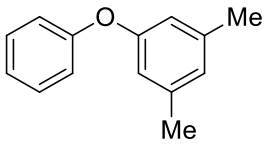
3-Methoxydiphenyl ether [1655-68-1]. **Table 2, entry 5:** The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and 3-iodoanisole (143 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Colorless oil. First run: 138 mg (69%). Second run: 142 mg (71%).



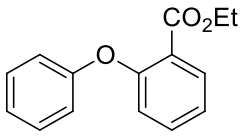
3-Cyanodiphenyl ether [50789-45-2]. Table 2, entry 6: The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (38.0 mg, 0.20 mmol), and 3-iodobenzonitrile (278 mg, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Yellowish oil. First run: 150 mg (77%). Second run: 150 mg (77%).



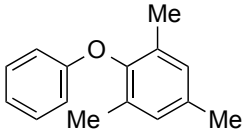
Ethyl 3-phenoxybenzoate [60677-14-7]. **Table 2, entry 7:** The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and ethyl 3-iodobenzoate (206 mg, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by four prep-TLC plates (silica gel; EtOAc). Colorless oil. First run: 128 mg (53%). Second run: 137 mg (57%).



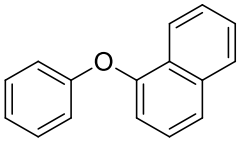
3,5-Dimethylphenyl phenyl ether [25539-14-4]. **Table 2, entry 8:** The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and 1-iodo-3,5-dimethylbenzene (175 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Colorless liquid. First run: 138 mg (70%). Second run: 139 mg (70%).



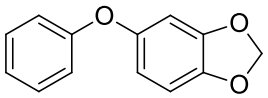
Ethyl 2-phenoxybenzoate [41755-76-4]. Table 2, entry 9: The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (38.0 mg, 0.20 mmol), and ethyl 2-iodobenzoate (203 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by four prep-TLC plates (silica gel; 5% EtOAc/hexanes). Colorless oil. First run: 147 mg (61%). Second run: 145 mg (60%).



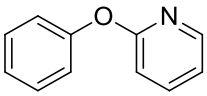
Phenyl 2,4,6-trimethylphenyl ether [61343-87-1]. **Table 2, entry 10:** The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (38.0 mg, 0.20 mmol), and 2-iodo-1,3,5-trimethylbenzene (298 mg, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Yellowish oil. First run: 125 mg (59%). Second run: 131 mg (62%).



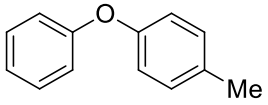
1-Naphthyl phenyl ether [3402-76-4]. Table 2, entry 11: The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (38.0 mg, 0.20 mmol), and 1-iodonaphthalene (180 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Yellowish solid. First run: 110 mg (50%). Second run: 114 mg (52%).



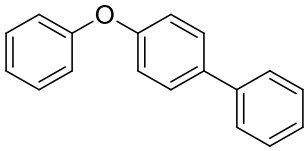
5-Phenoxybenzo[*d*][1,3]dioxole [150092-68-5]. **Table 2, entry 12:** The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (38.0 mg, 0.20 mmol), and 5-iodo-1,3-benzodioxole (157 mg, 1.20 mmol; filtered through a plug of silica prior to use). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by four prep-TLC plates (5% EtOAc/hexanes). Colorless oil. First run: 112 mg (52%). Second run: 112 mg (52%).



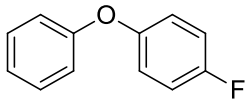
Phenyl 2-pyridyl ether [4783-68-0]. Table 2, entry 13: The title compound was synthesized according to the General Procedure from phenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodopyridine (130 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (1% EtOAc/hexane). White solid. First run: 132 mg (77%). Second run: 129 mg (75%).



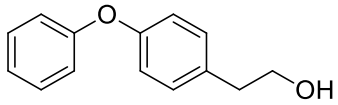
4-Methylphenyl phenyl ether [1706-12-3]. Table 3, entry 1: The title compound was synthesized according to the General Procedure from *p*-cresol (109 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Colorless oil. First run: 113 mg (61%). Second run: 111 mg (59%).



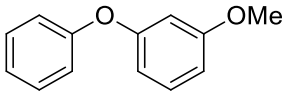
4-Phenylphenyl phenyl ether [3933-94-6]. Table 3, entry 2: The title compound was synthesized according to the General Procedure from 4-phenylphenol (96 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). White solid. First run: 167 mg (68%). Second run: 172 mg (71%).



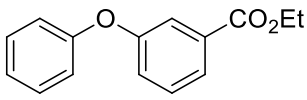
4-Fluorophenyl phenyl ether [330-84-7]. Table 3, entry 3: The title compound was synthesized according to the General Procedure from 4-fluorophenol (113 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Colorless oil. First run: 129 mg (69%). Second run: 122 mg (65%).



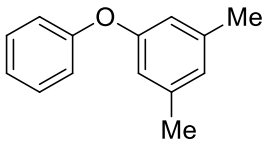
2-(4-Phenyloxyphenyl)ethyl alcohol [52446-51-2]. Table 3, entry 4: The title compound was synthesized according to the General Procedure from 4-(2-hydroxyethyl)phenol (141 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (20% EtOAc/hexane). Colorless oil. First run: 139 mg (65%). Second run: 150 mg (70%).



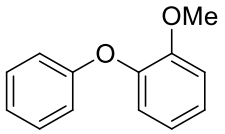
3-Methoxydiphenyl ether [1655-68-1]. **Table 3, entry 5:** The title compound was synthesized according to the General Procedure from 3-methoxyphenol (114 μL, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (5% EtOAc/hexane) and purified by column chromatography on silica gel (hexane). Colorless oil. First run: 153 mg (76%). Second run: 153 mg (76%).



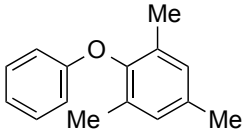
Ethyl 3-phenoxybenzoate [60677-14-7]. **Table 3, entry 6:** The title compound was synthesized according to the General Procedure from ethyl 3-hydroxybenzoate (168 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (1% EtOAc/hexane). Colorless oil. First run: 148 mg (61%). Second run: 150 mg (62%).



3,5-Dimethylphenyl phenyl ether [25539-14-4]. **Table 3, entry 7:** The title compound was synthesized according to the General Procedure from 3,5-dimethylphenol (123 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Colorless liquid. First run: 140 mg (71%). Second run: 131 mg (66%).



2-Methoxyphenyl phenyl ether [1695-04-1]. Table 3, entry 8: The title compound was synthesized according to the General Procedure from 2-methoxyphenol (112 μL, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). White solid. First run: 134 mg (67%). Second run: 126 mg (63%).



Phenyl 2,4,6-trimethylphenyl ether [61343-87-1]. **Table 3, entry 9:** The title compound was synthesized according to the General Procedure from 2,4,6-trimethylphenol (138 mg, 1.00 mmol), DBU (152 μL, 1.00 mmol), KO*t*-Bu (56 mg, 0.50 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (137 μL, 1.20 mmol). The reaction mixture was filtered through a plug of silica gel (EtOAc) and purified by column chromatography on silica gel (hexane). Yellowish oil. First run: 122 mg (57%). Second run: 124 mg (58%).

Eqn (3). Under an atmosphere of N_2, a tube was charged with $[Cu(OPh)_2][N(Bu)_4]$ (9.8 mg, 0.020 mmol, 1.0 equiv), and then a solution of 3-iodotoluene (8.7 mg, 0.040 mmol, 2.0 equiv) and DBU (6.0 μL, 0.040 mmol, 2.0 equiv) in MeCN (1.0 mL) was added. The tube was sealed with a rubber septum, the joint was wrapped with electrical tape, and the quartz tube was transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm for 3 h. The yield of product was determined by GC analysis.

Eqn (5). Under an atmosphere of N_2, a tube was charged with $[Cu(OPh)_2][N(Bu)_4]$ (9.8 mg, 0.020 mmol, 1.0 equiv), and then a solution of benzene diazonium tetrafluoroborate (3.8 mg, 0.020 mmol, 1.0 equiv) and $Ru(bpy)_3(PF_6)_2$ (17.2 mg, 0.020 mmol, 1.0 equiv) in MeCN (1.0 mL) was added. The tube was sealed with a rubber septum, the joint was wrapped with electrical

tape, and the quartz tube was irradiated under CFL for 12 h. The yield of product was determined by GC analysis.

III. ^{1}H NMR Spectra

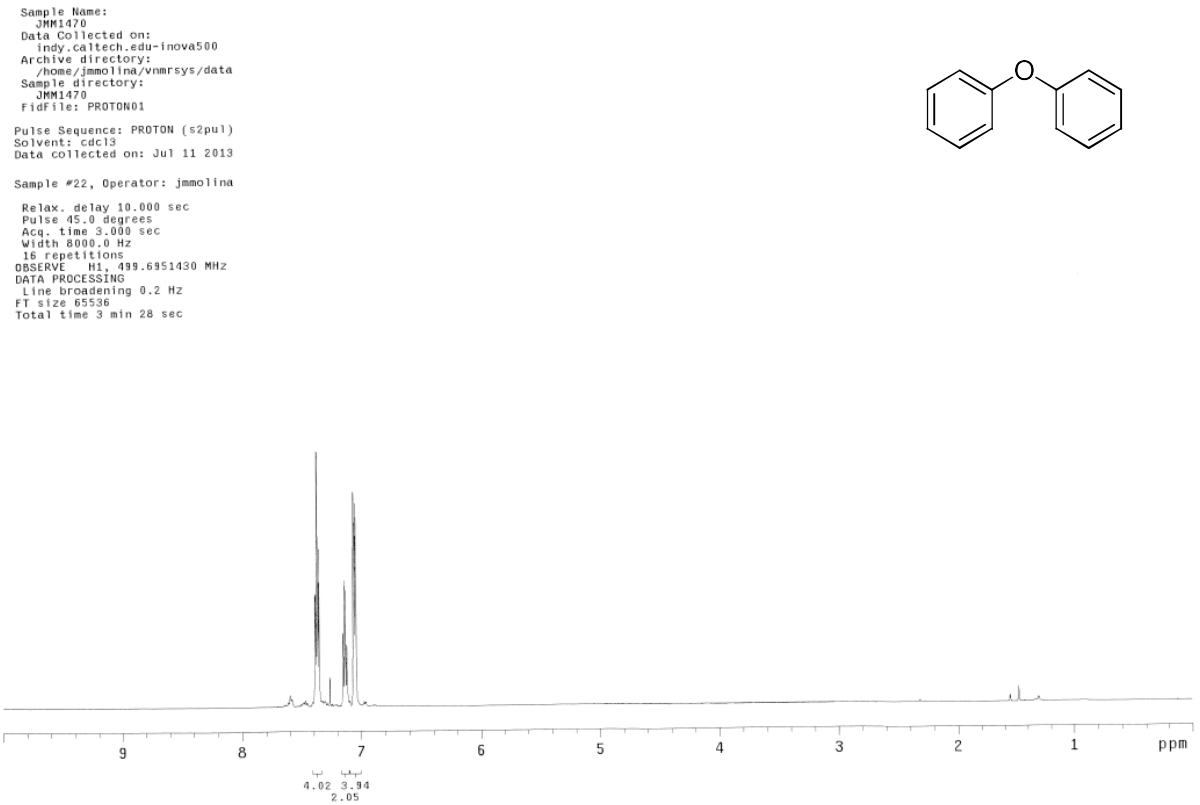


Figure S1. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 1.

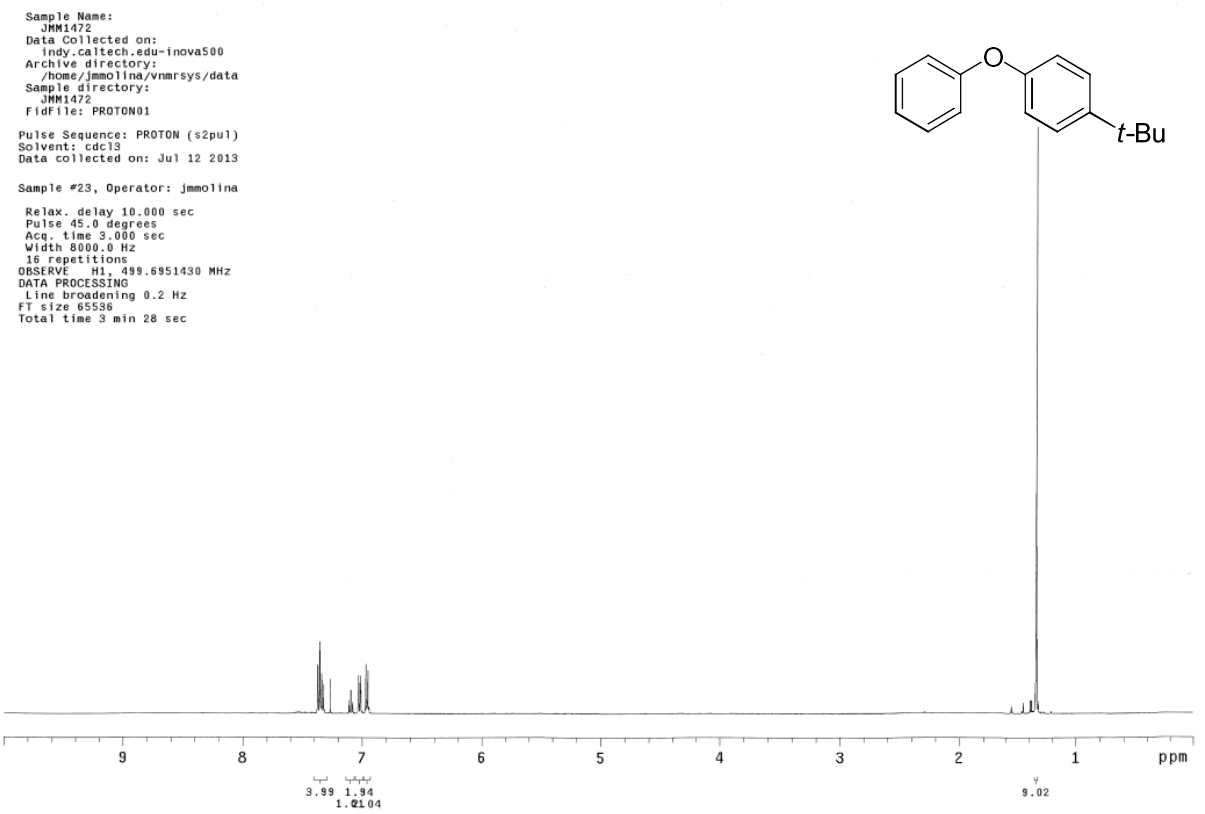


Figure S2. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 2.

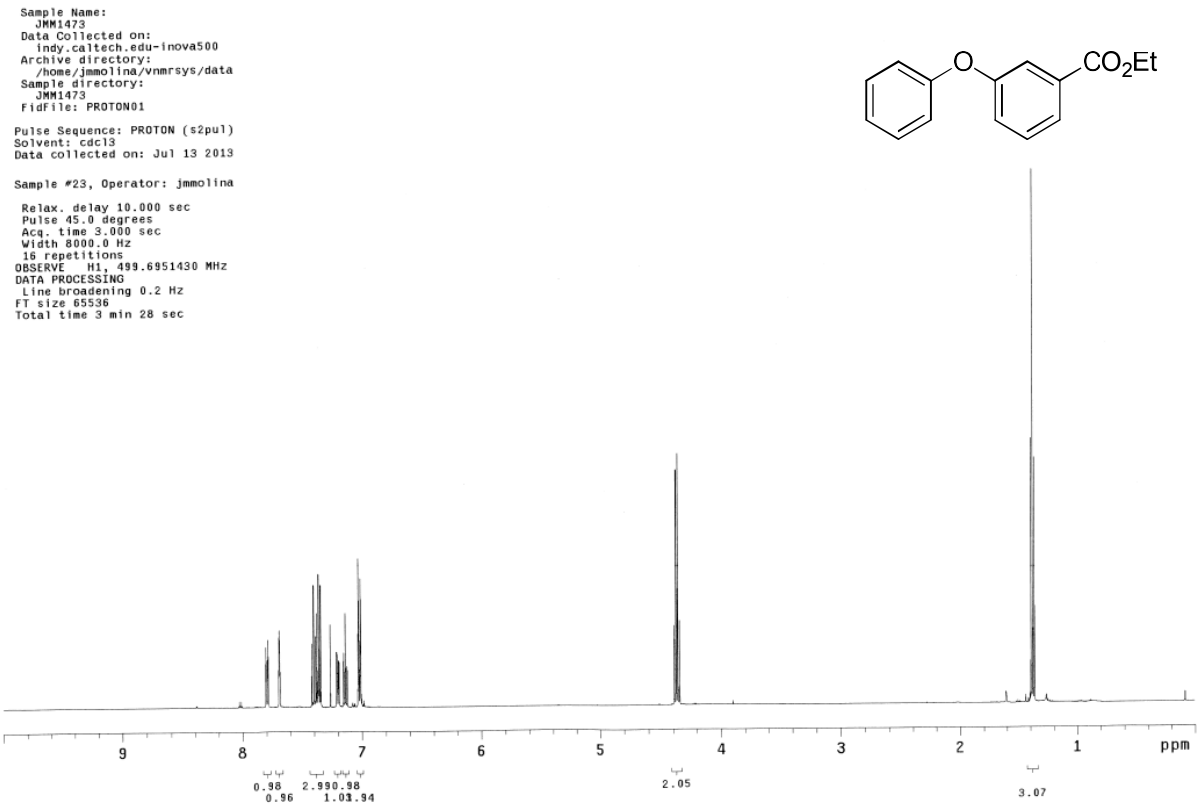


Figure S3. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 3.

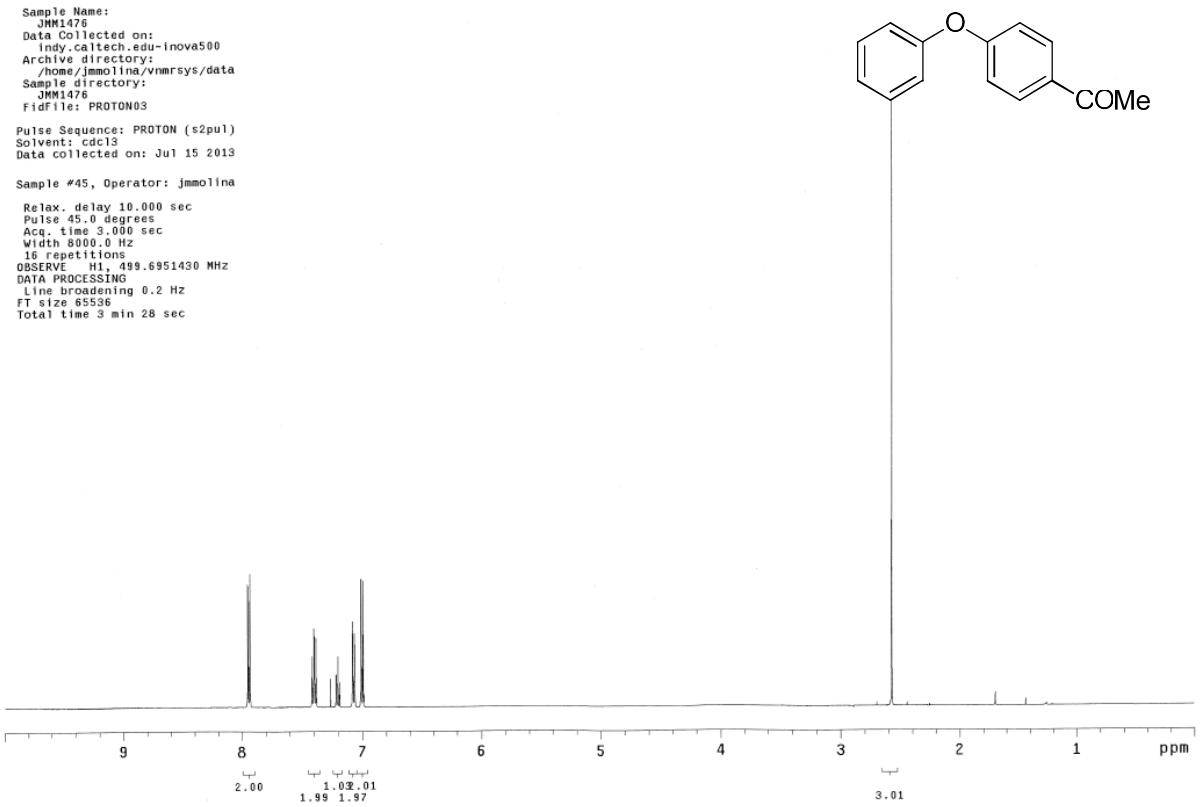


Figure S4. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 4.

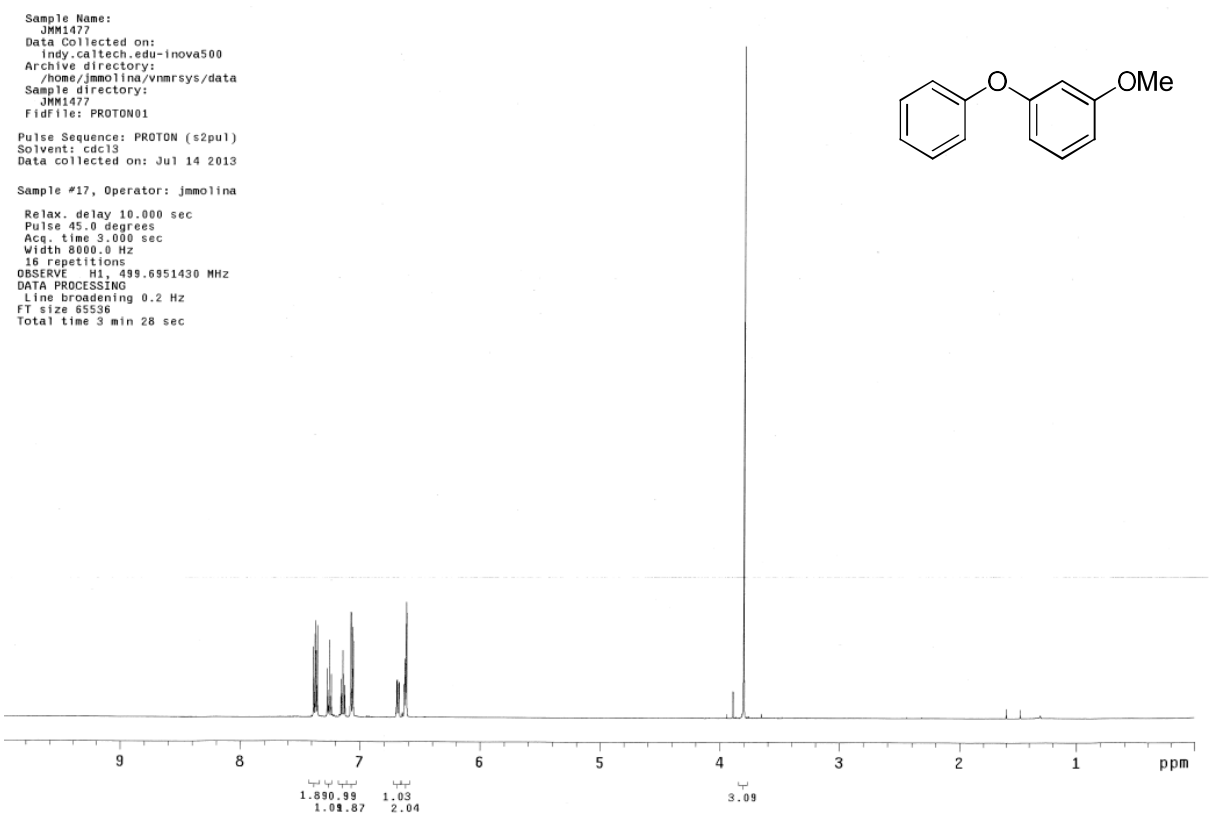


Figure S5. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 5.

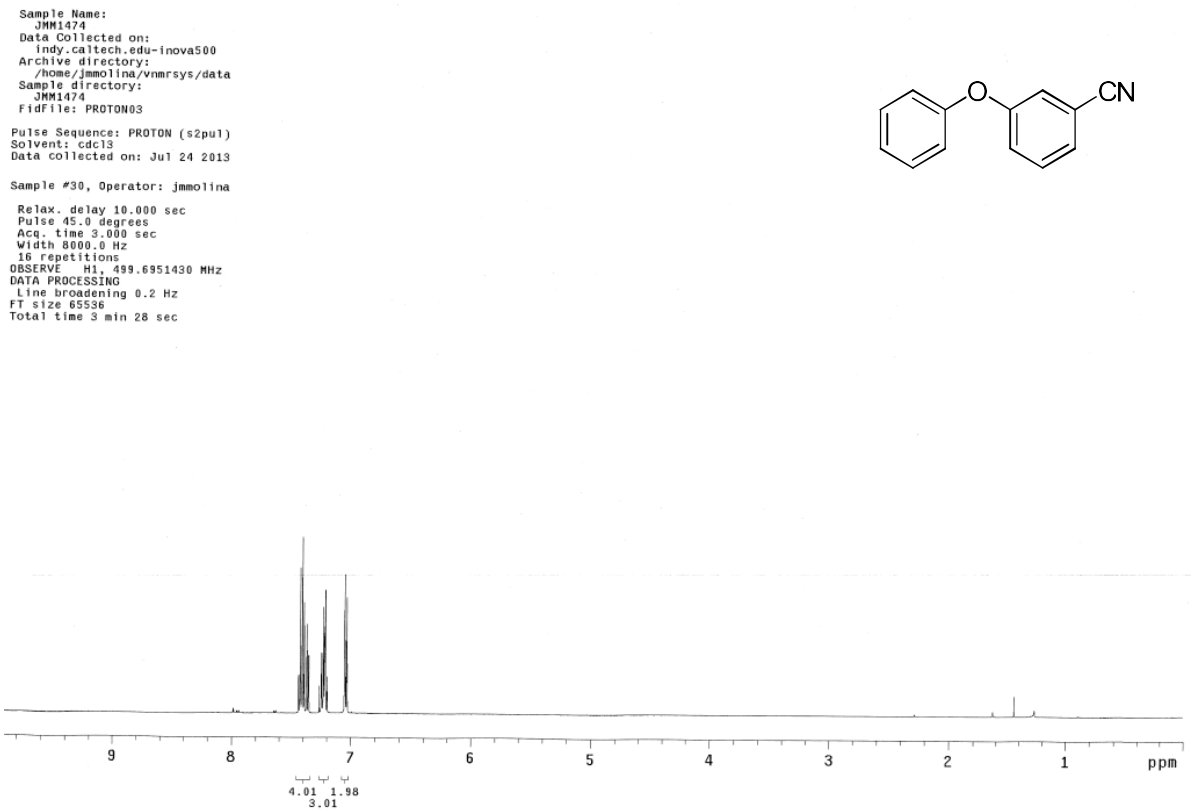


Figure S6. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 6.

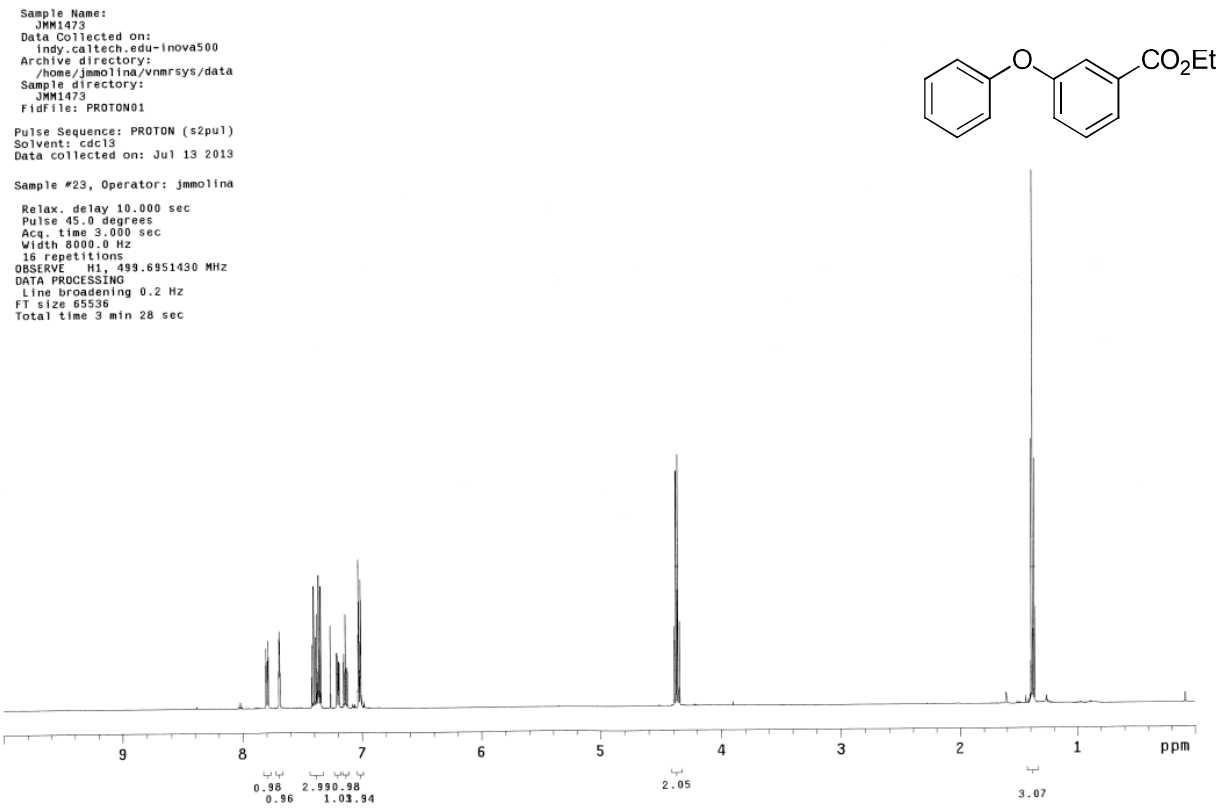


Figure S7. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 7.

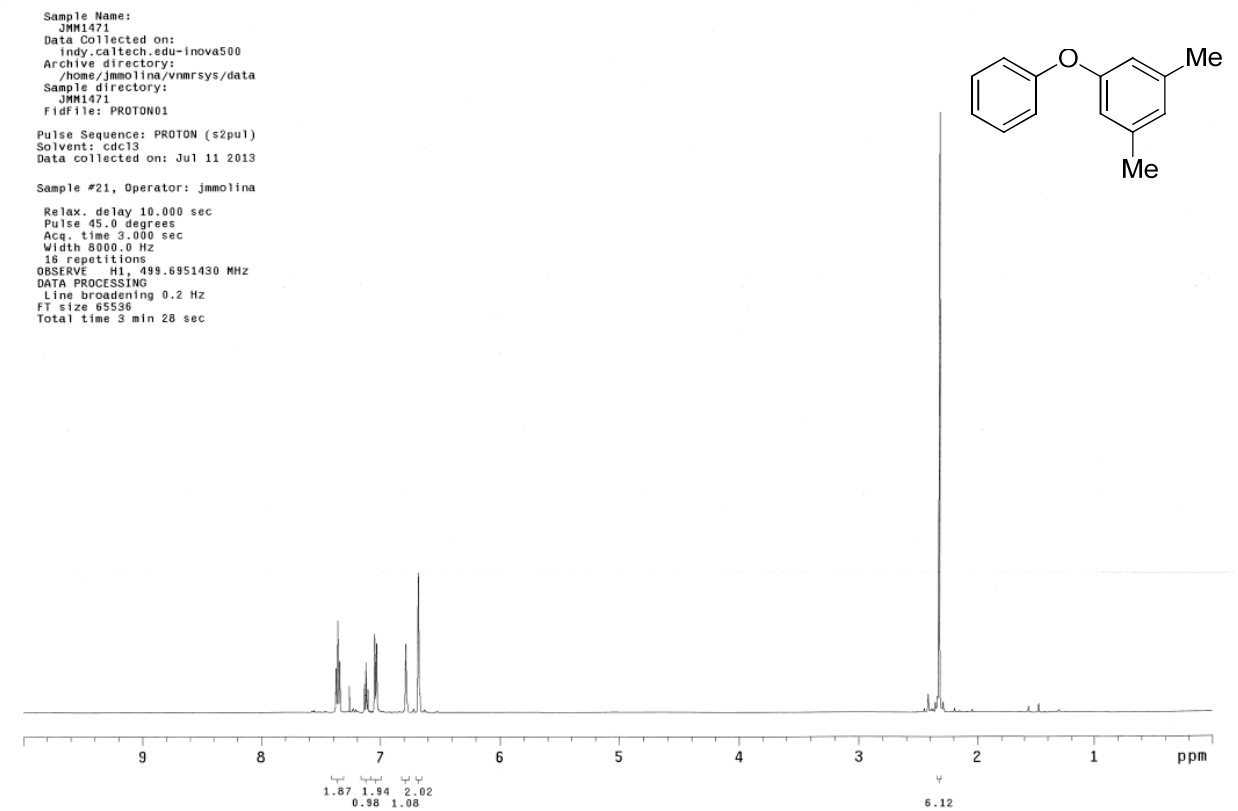


Figure S8. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 8.

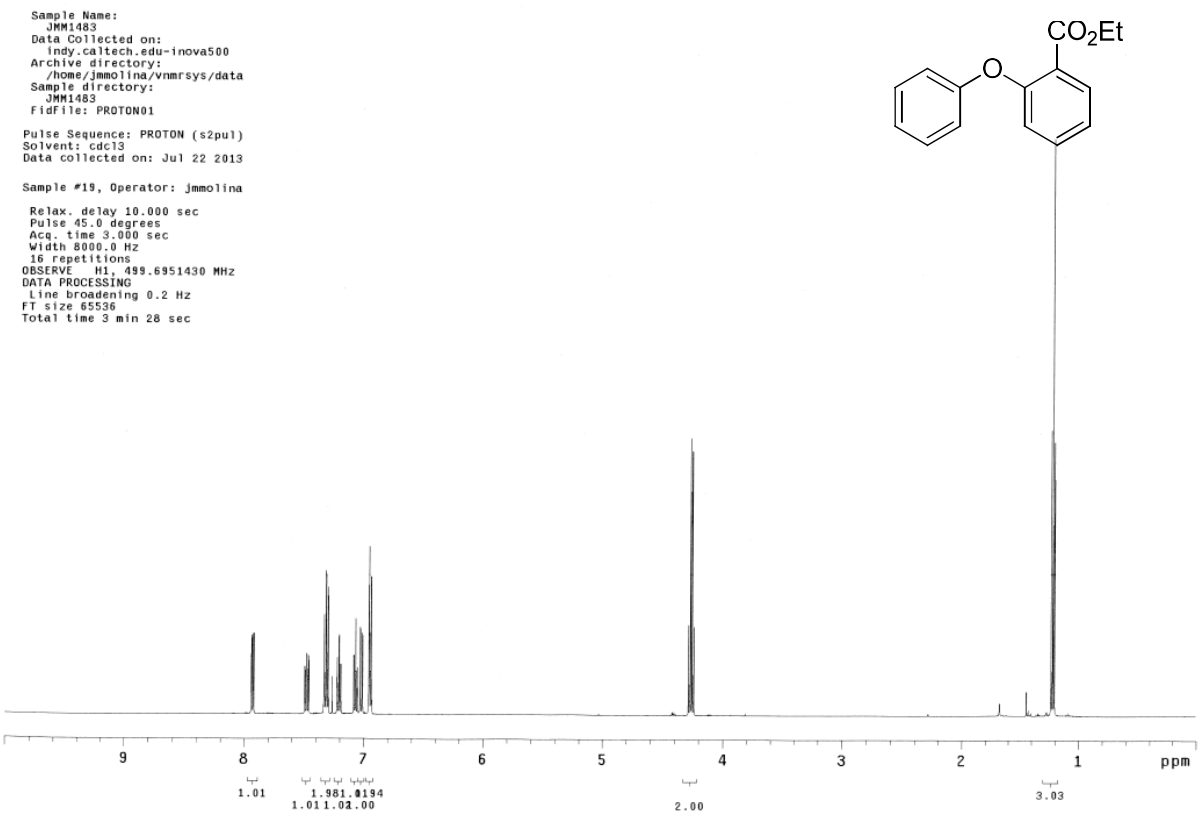


Figure S9. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 9.

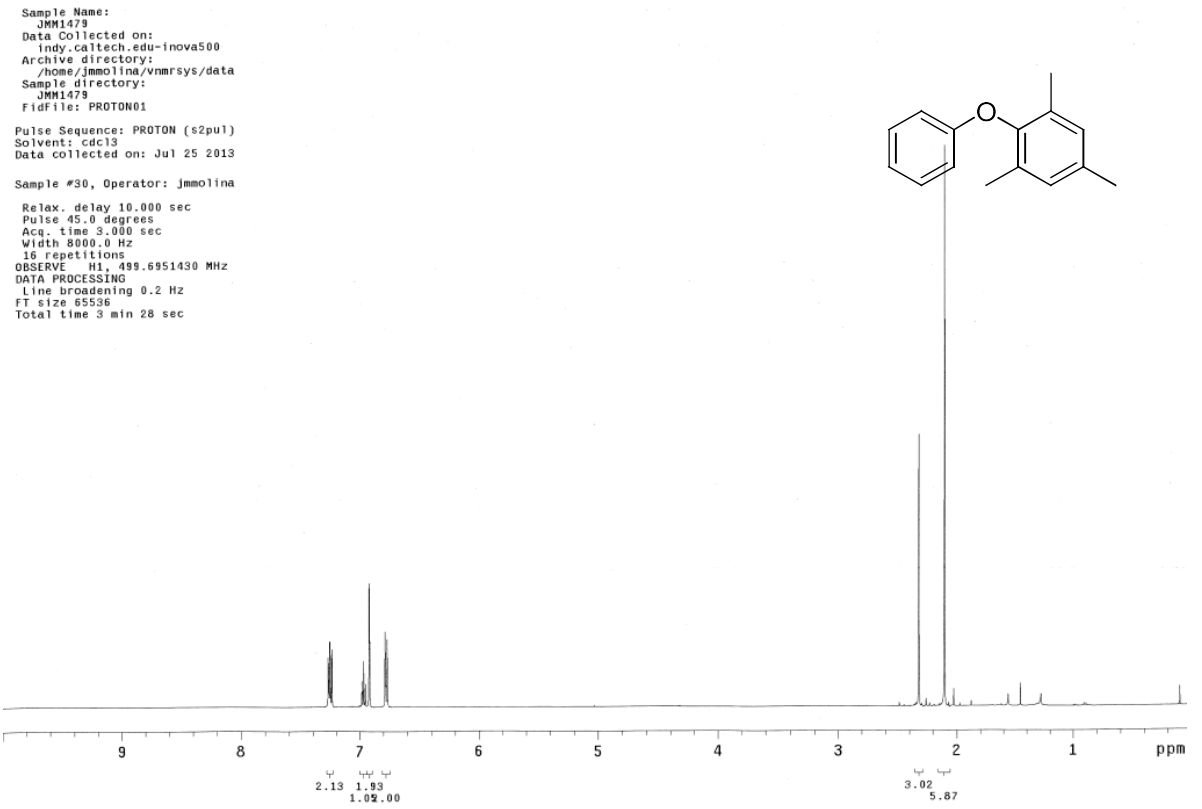


Figure S10. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 10.

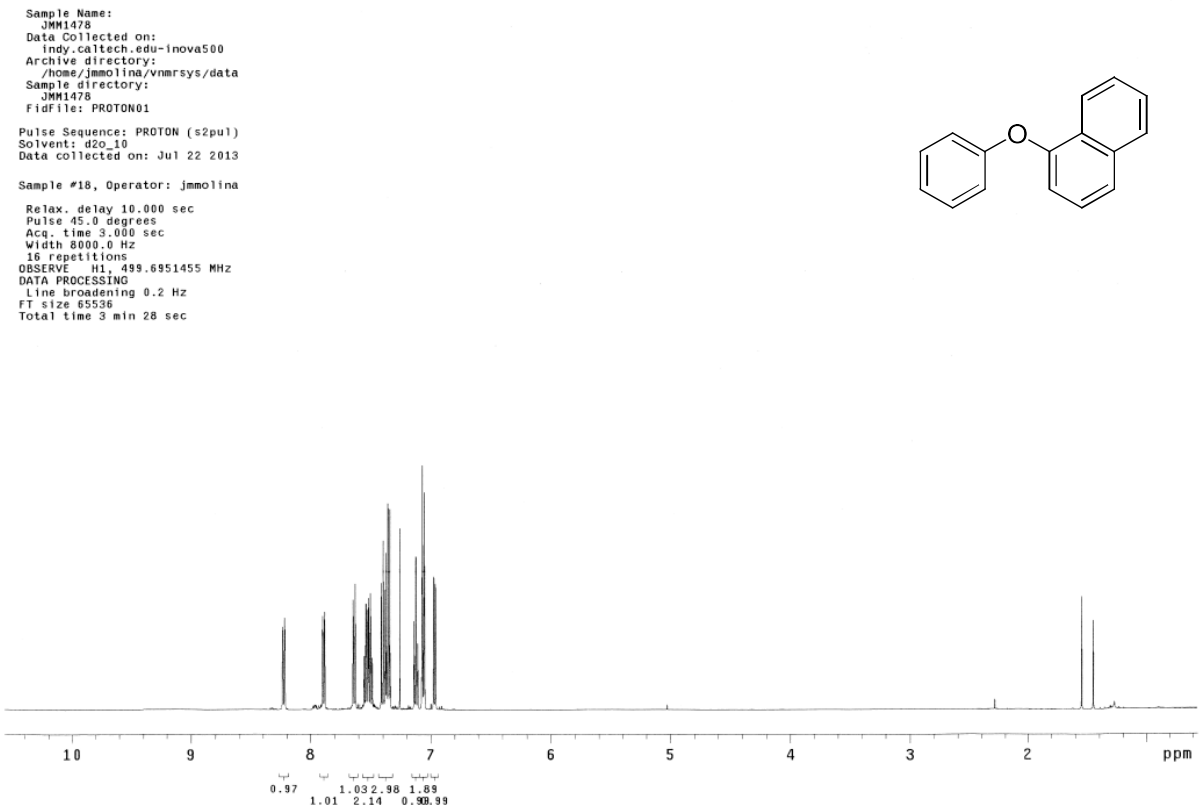


Figure S11. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 11.

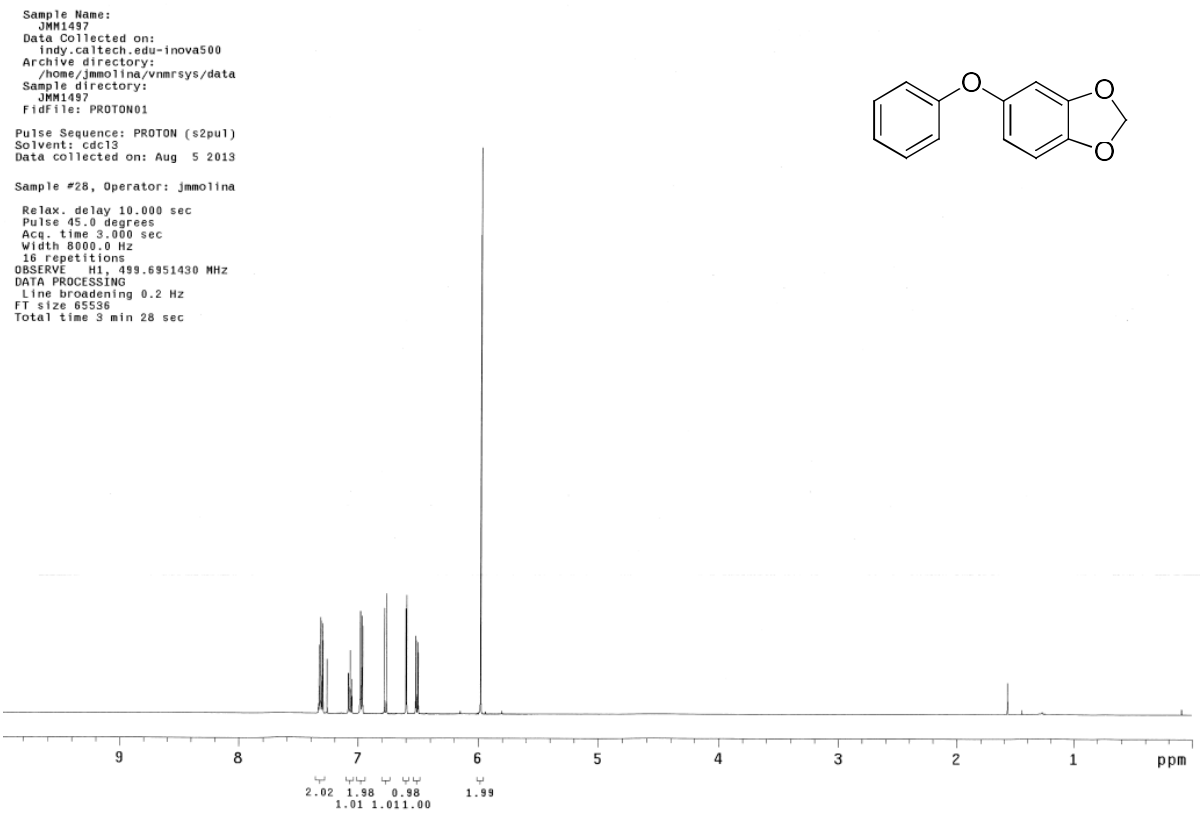


Figure S12. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 12.

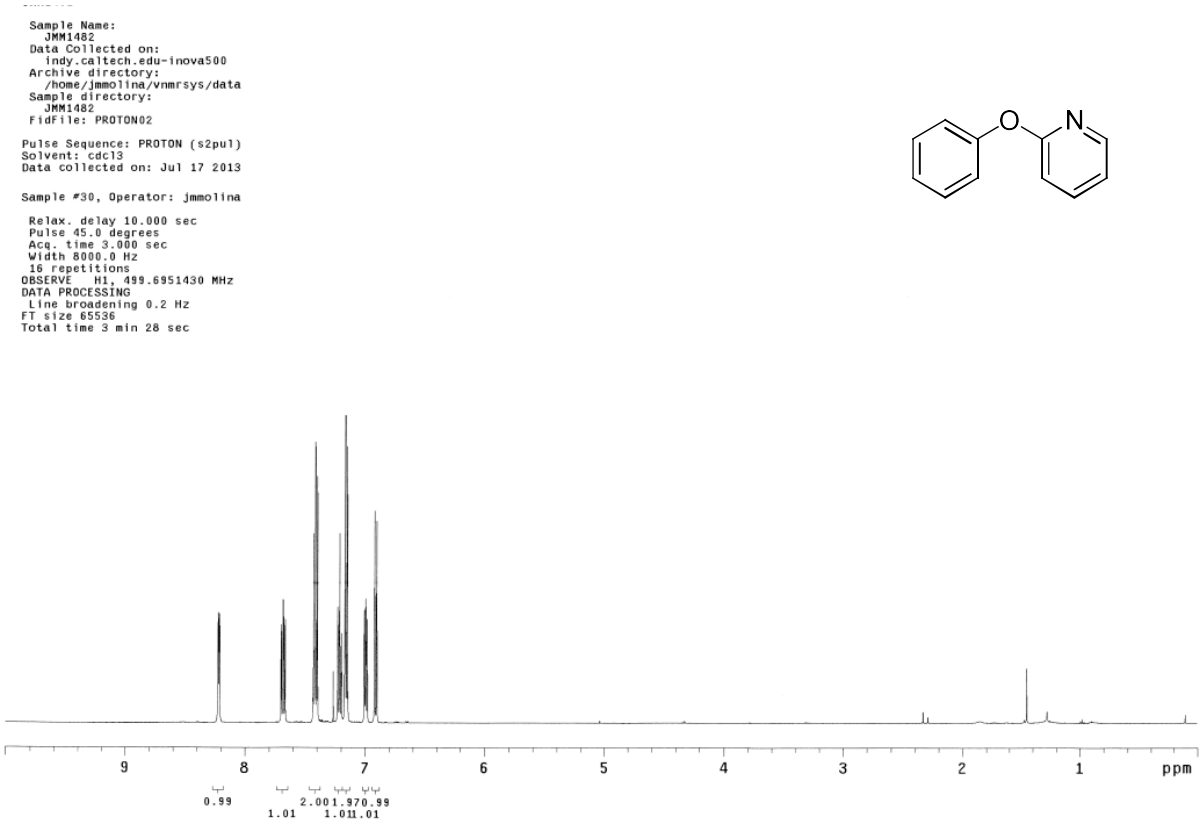


Figure S13. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 13.

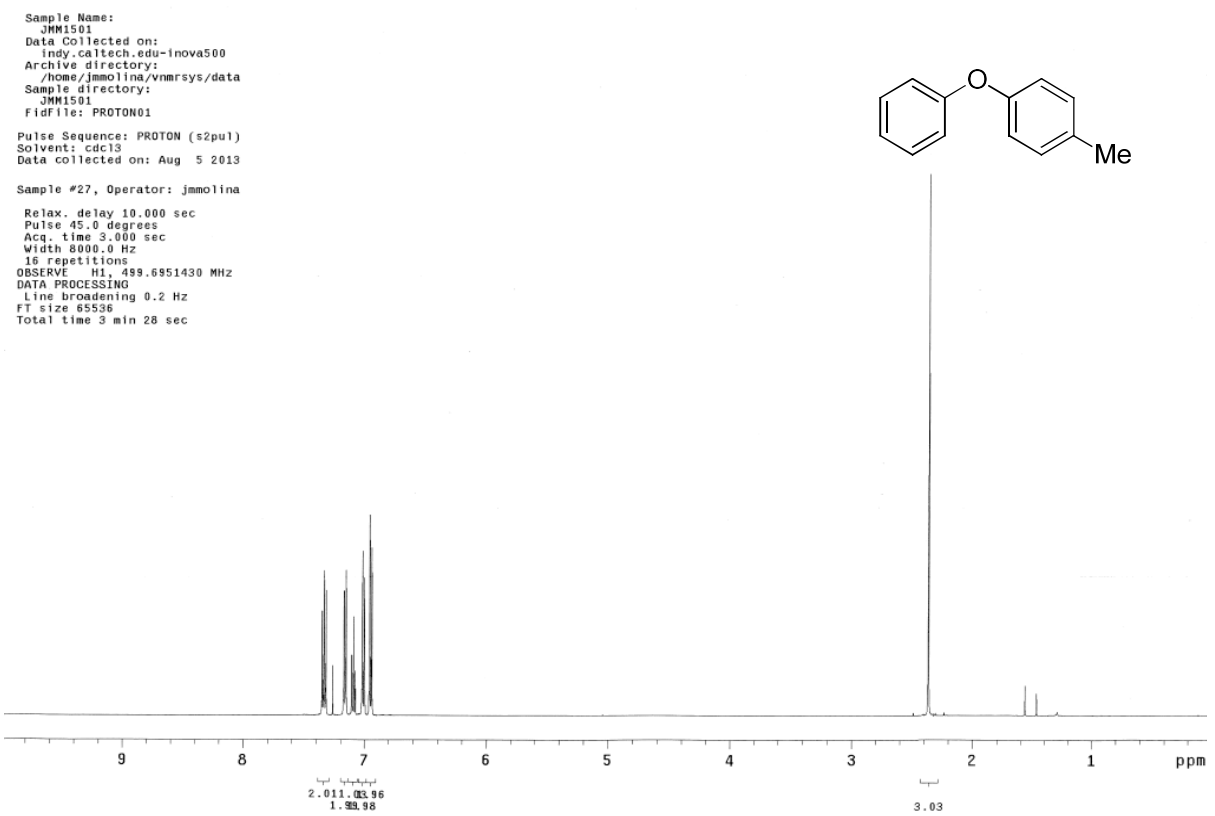


Figure S14. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 1.

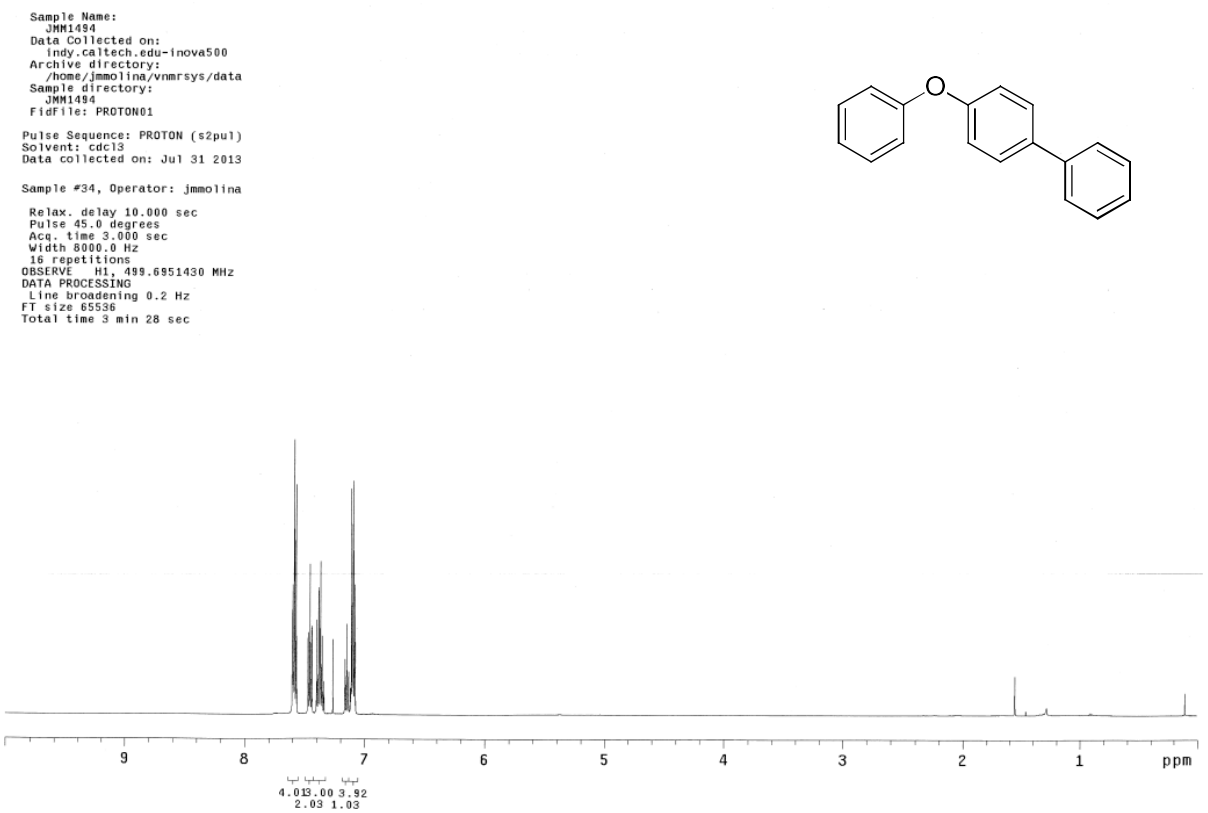


Figure S15. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 2.

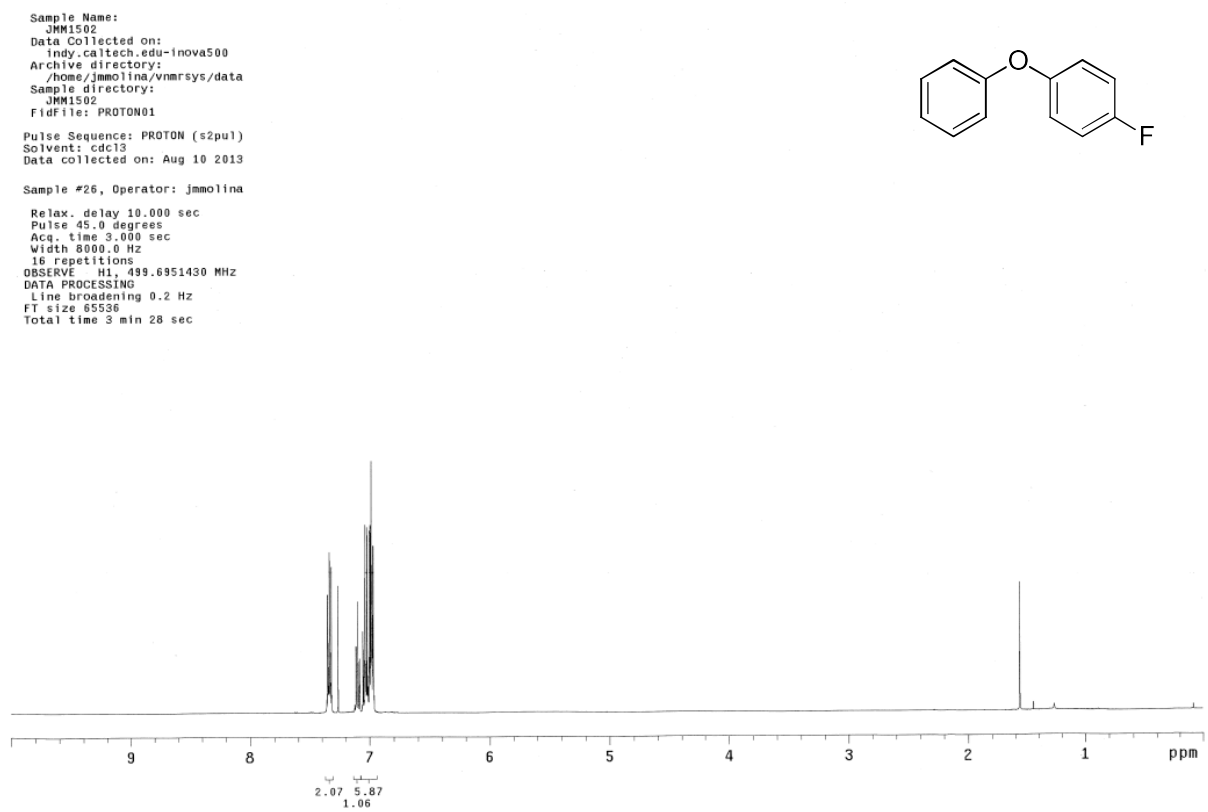


Figure S16. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 3.

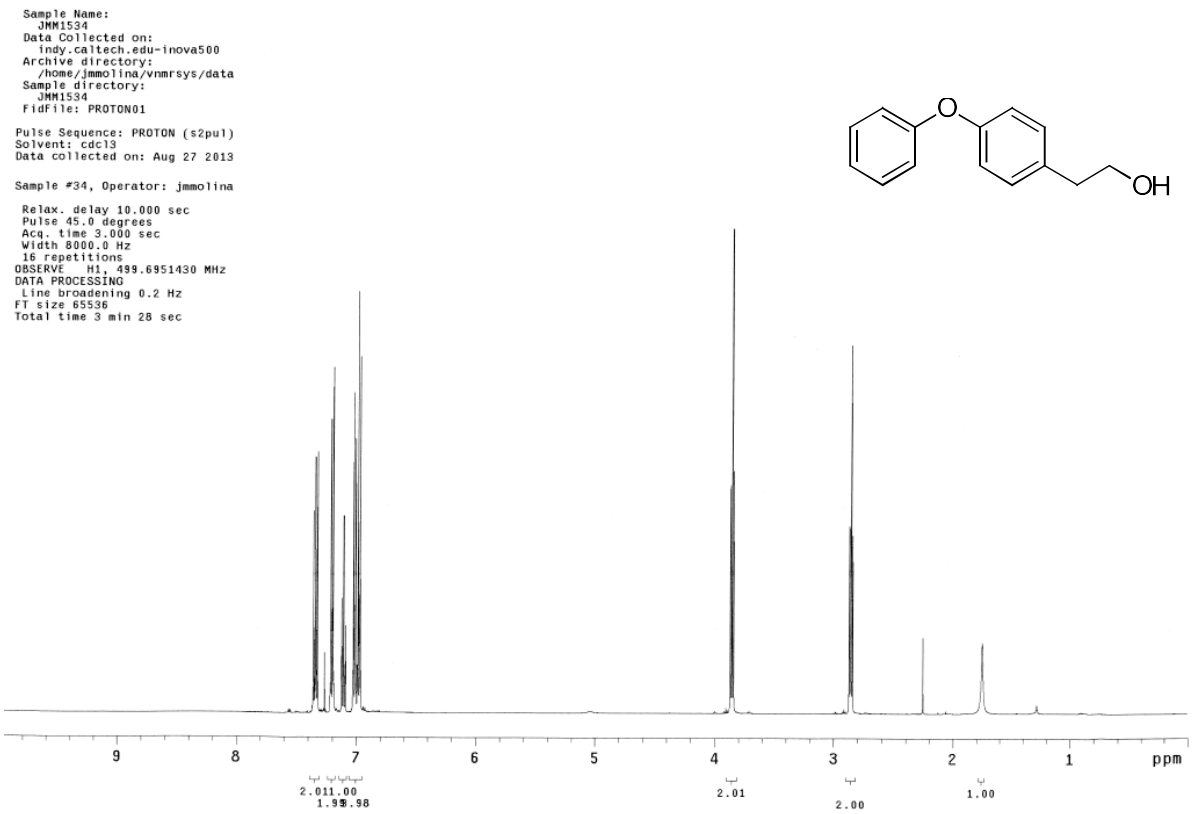


Figure S17. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 4.

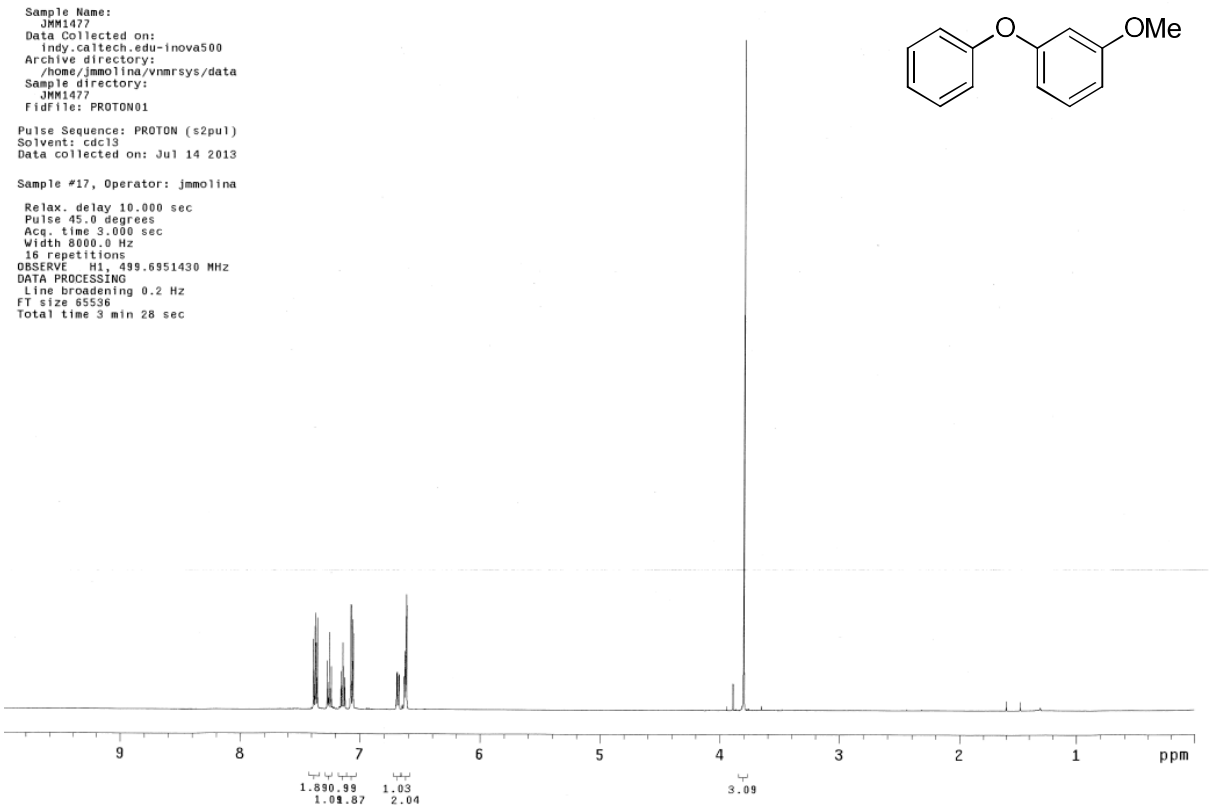


Figure S18. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 5.

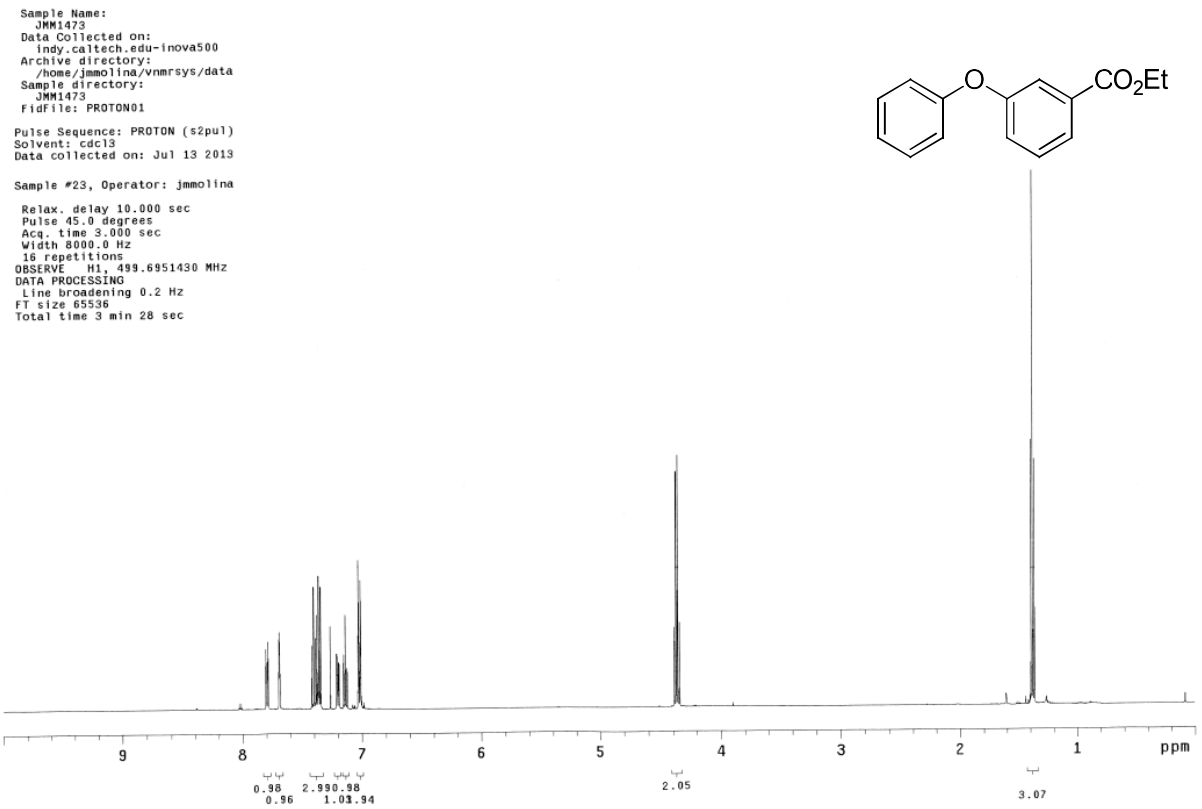


Figure S19. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 6.

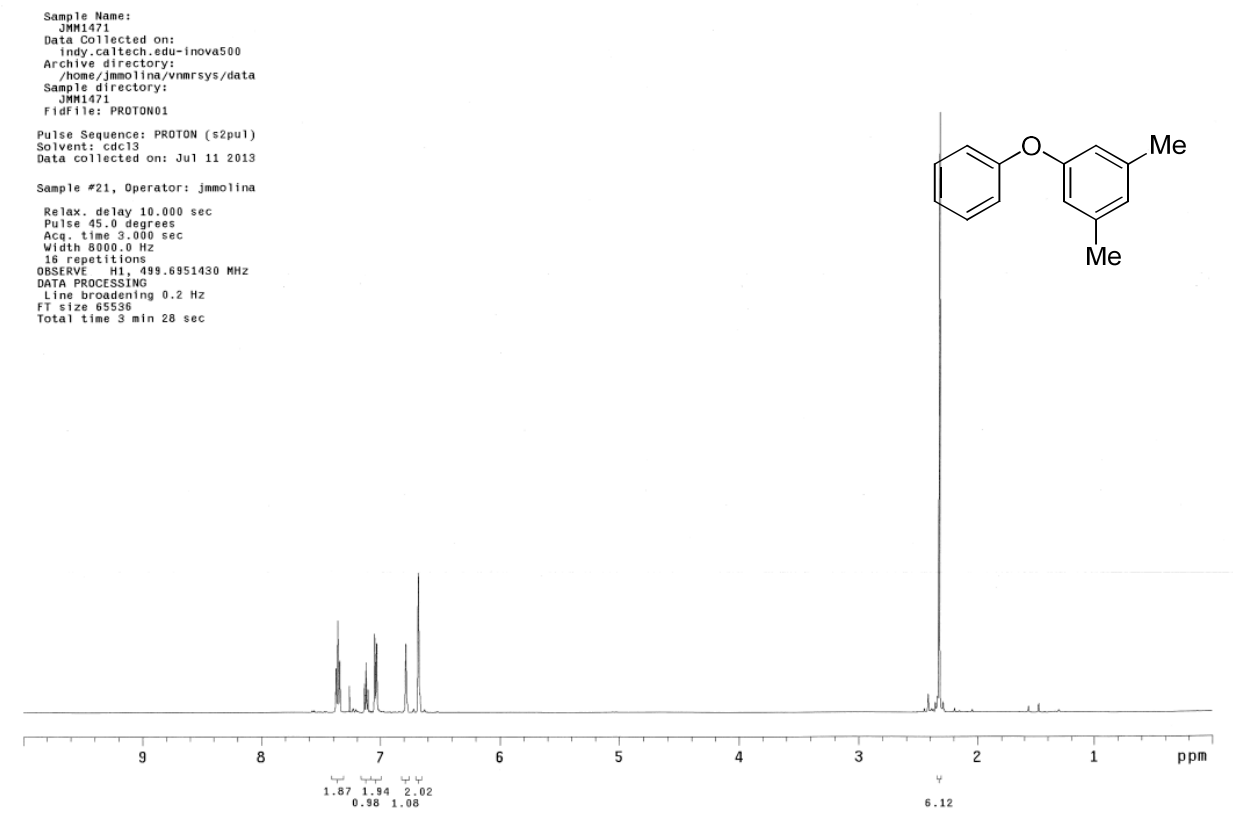


Figure S20. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 7.

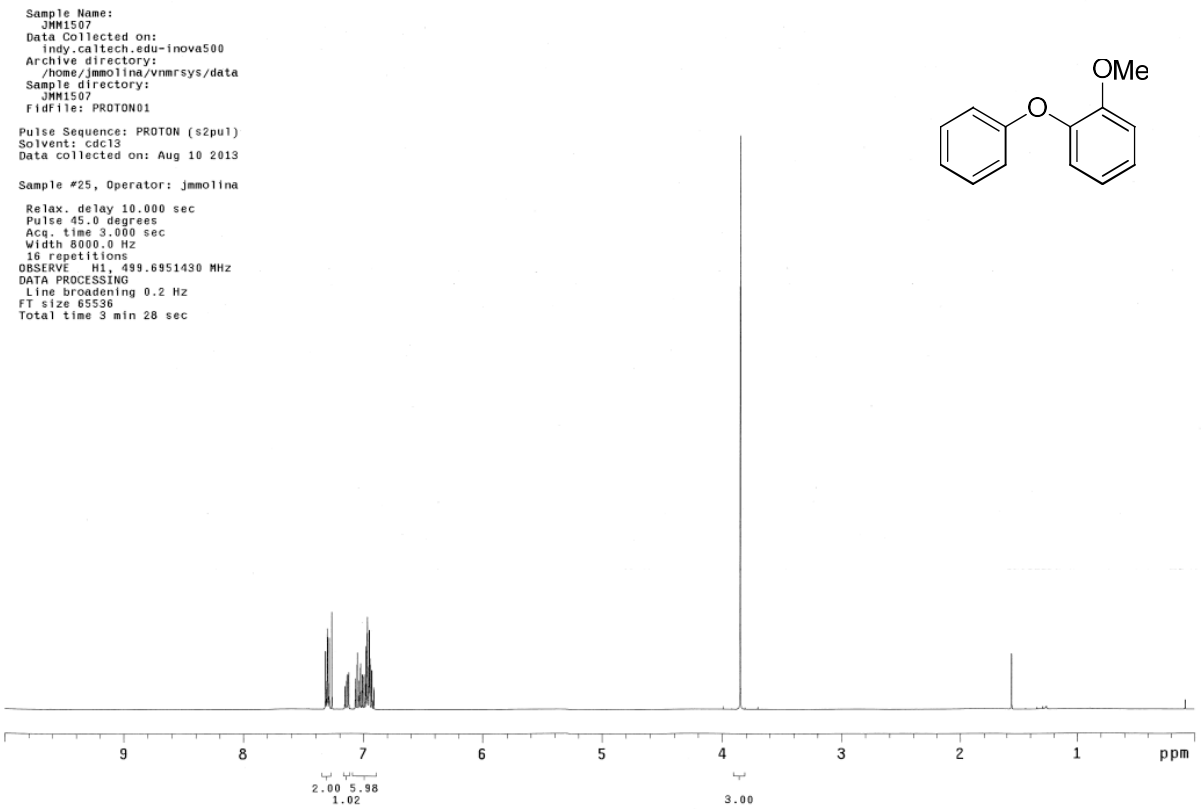


Figure S21. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 8.

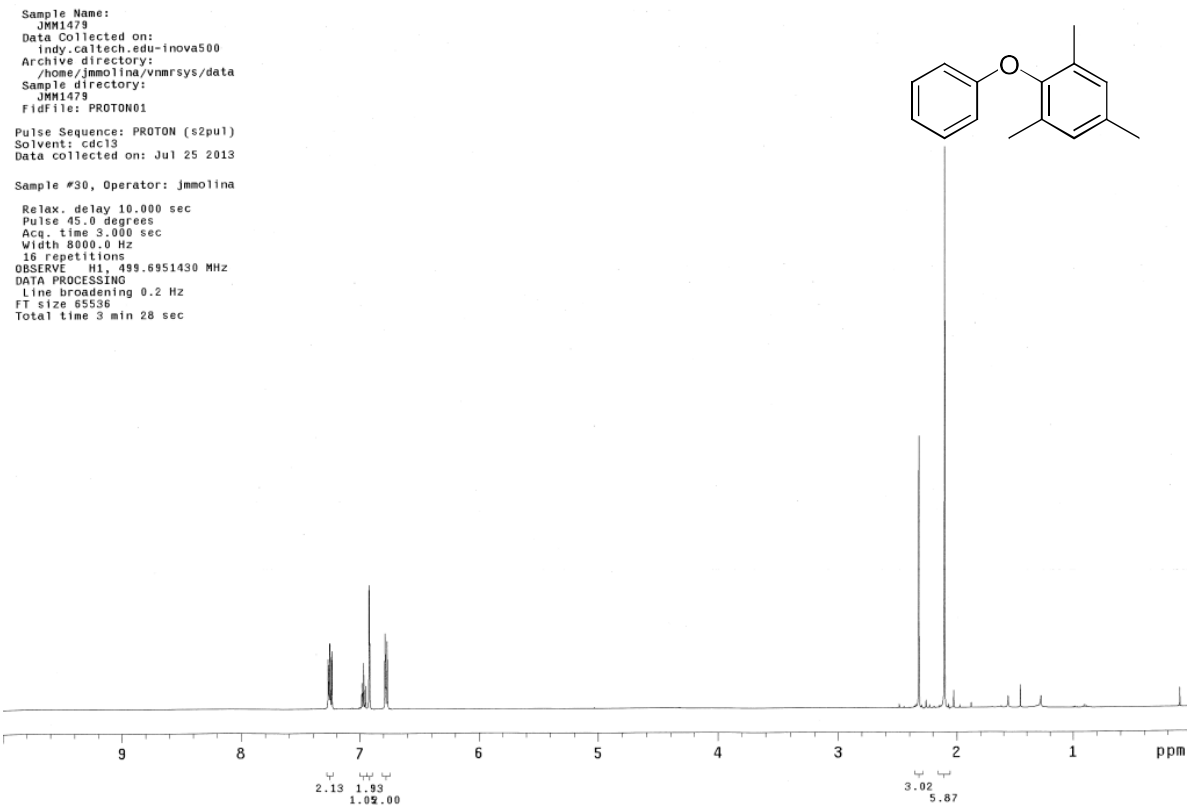


Figure S22. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 9.

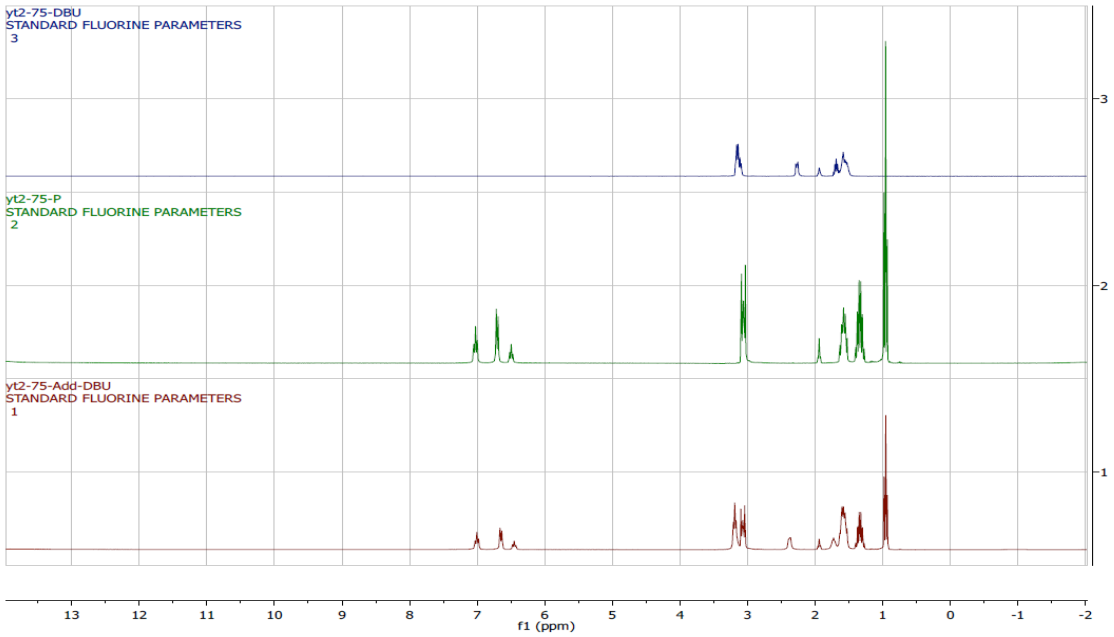


Figure S23. Stacked ^{1}H NMR spectrum (MeCN-d^{3}) for Complex **1**, free DBU and the (1:1) mixture.